AMENDMENTS TO THE DRAWINGS

The attached two sheets replace the figure at page 2 of the PCT specification, now indicated as Fig. 1, and the figure at page 5 of the PCT specification, now indicated as Fig. 2. The only changes are an improvement in reading quality. No new matter has been added.

Attachment: Replacement Sheets

Annotated Sheets Showing Changes

REMARKS/ARGUMENTS

A. In the Information Disclosure Statement

Reference is section 1 of the Office Action, wherein the Examiner has stated that the references cited in the Search Report have not been considered.

The Examiner is respectfully directed to MPEP § 1844 stating, in relevant part:

> *The search report* will be published by the International Bureau and, together with the written opinion of the International Searching Authority, *will serve as a basis for the examination of the international application by the designated Offices* and the International Preliminary Examining Authority.

(emphasis added).

Because the USPTO is acting as a designated office, under the definition of 37 CFR 1.414, Applicant has not provided an Information Disclosure Statement ("IDS") in good faith, under the expectation that the Examiner would rely on the search report.

The Examiner has independently relied on two of the references cited in the search report, therefore, this issue is moot as to those two references. For the other references, Applicant is providing an IDS, wherein foreign references have been converted to the relative U.S. patents or patent applications whenever available. Applicant is respectfully requesting that such IDS be made of record.

B. In the Specification

Reference is sections 2, 3, and 4 of the Office Action. A marked-up copy and a clean copy of a substitute specification are enclosed to the present amendment, and entry into the record is respectfully requested.

The title of the substitute specification is as in the original PCT application, while the published application US 2005/0171376 A1 reported an incorrectly spelled title.

Various changes have been introduced throughout the specification to make it consistent with modern US English usage, and section headings have been added to conform to USPTO formatting requirements.

Further, the abstract has been expanded to capture an embodiment of the invention with greater detail, and the drawings at pp. 2 and 4 of the PCT published application have been redrawn and are now indicated as Figs. 1-2. The formula at page 10 has also been rewritten.

No new matter has been added.

C. In the Claims

Claims 1-7 are pending in the present application. Claims 1 and 5-7 have been canceled, and new claims 8-12 have been introduced. Therefore, upon entry of the present amendment, claims 2-4 and 8-12 will be subject to examination.

1. Introduction

Claims 2-4 have been amended to overcome the Examiner's objections and rejections, and have also been amended to point out the invention with greater clarity in relation to all the references cited in the international search report.

New claims 8-9 are directed at specific embodiments of the invention at claim 2. New claims 10-12 are directed at methods for inhibiting scale formation that incorporate the polymethylenephosphonate derivative of claim 2.

2. Regarding the Claim Rejections under 35 USC § 101 and 112

Reference are sections 5-10 of the Office Action.

Because claims 5-7 have been canceled, the issues raised by the Examiner as to those claims are now moot.

As requested by the Examiner, the term "con" has been replaced with "wherein," the division sign with a colon has been removed, and the different "R" groups have been distinguished with a subscript number.

Concerning the rejection of claim 3 at section 10 of the Office Action, the language of claim 3 has been modified to point out more distinctly that the groups listed in claim 3 replace at least one of the $CH_2PO_3M_2$ groups at the end of the molecular chain claimed in claim 2.

Based on the above discussion, Applicant respectfully requests the removal of the rejections under 35 U.S.C. 101 and 112.

3. Regarding the Rejections under 35 USC 102(b)

a. The rejections of claims 2 and 4 as allegedly anticipated by EP 0479462-A1 to Stewart at al. ("Stewart") is respectfully traversed. Because claim 1 has been canceled, the rejection of claim 1 is moot.

Stewart teaches a method for inhibiting scale formation with the use of a phosphonate having a composition described on page 1 of the Stewart patent. The Examiner has made particular reference to entry 13 in the table at page 7 of Stewart.

Each of the general formula at page 1, of the variations described at pages 3, 4, 5, 10, and 11 of Stewart, and of the specific example cited by the Examiner involve the use of a double $-CHR^1PO_3R_2$ group at each end of the molecule chain, while Applicant discloses a single group at each end of the chain, as shown in amended Claim 2.

Therefore, Stewart does not anticipate Applicant's invention, and the removal of the 35 USC 102(b) rejection of claim 2 as to the Stewart reference is respectfully requested. Because claim 4 is dependent on now allowable claim 2, claim 4 is also now allowable.

b. The rejection of claim 2 as allegedly anticipated by GB 1,392,044 to Harris et al. ("Harris") is respectfully traversed. Because claim 1 has been canceled, the rejection of claim 1 is now moot.

Harris discloses a composition for inhibiting the corrosion of metal surfaces. The Examiner has specifically cited entries 17-19 in the table at page 10.

In order to overcome this rejection, Applicant has modified claim 2 to include the language: "wherein at least one of R_1, R_2, and R_3 is not $CH_2PO_3M_2$." This renders Applicant's invention patentably different form Harris. As further detailed in claim 2, none of the R_1, R_2, and R_3 groups may be hydrogen, further differentiating Applicant's invention from Harris.

Therefore, Harris does not anticipate Applicant's invention, and the removal of the 35 USC 102(b) rejection as to the Harris reference is respectfully requested.

4. Regarding the Claim Objections

Reference is section 13 of the Office Action. In response to the Examiner's objections, claim 3 has been corrected as requested.

D. In the Drawings

The attached two sheets of drawings replace the figure at page 2 of the PCT specification, now indicated as Fig. 1, and the figure at page 5 of the PCT specification, now indicated as Fig. 2. The only changes from the original specification are an improvement in reading quality. No new matter has been added.

CONCLUSION

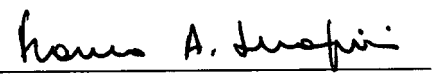
In view of the amendments and remarks submitted herein, Applicant respectfully requests that a timely Notice of Allowance be issued in this case.

If it is felt that direct communication would serve to advance prosecution of the present application, the Examiner is invited to contact the undersigned attorney of record, Franco A. Serafini, by telephone, fax, or e-mail.

Dated: October 18, 2005

Respectfully submitted,

SERAFINI ASSOCIATES

By 

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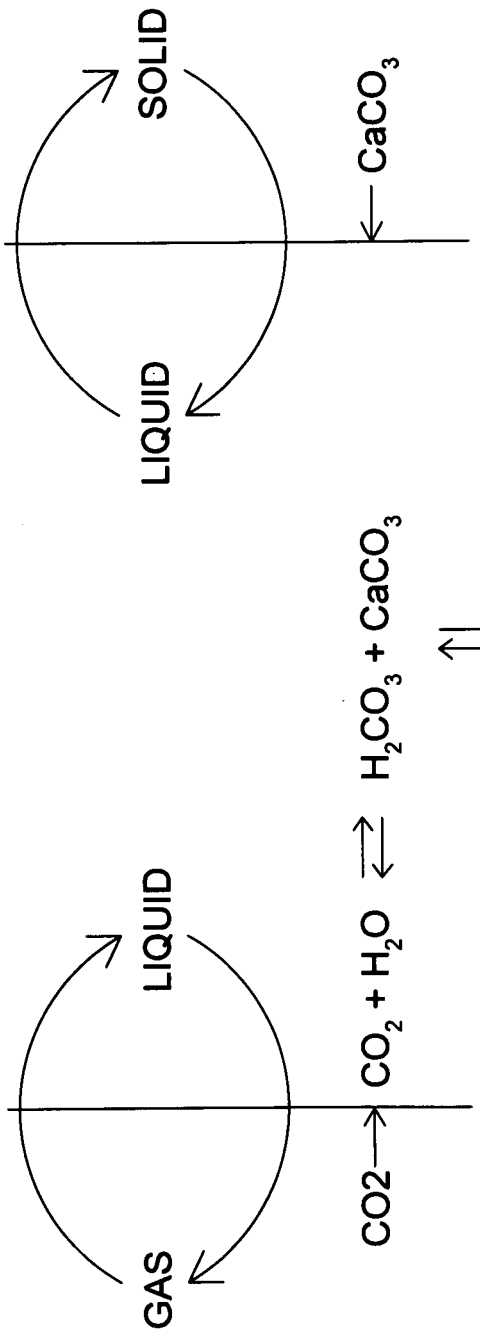


REDRAWN FOR IMPROVED CLARITY. NO NEW MATTER ADDED.

Fig. 1

REDRAWN FOR IMPROVED CLARITY. NO NEW MATTER ADDED.

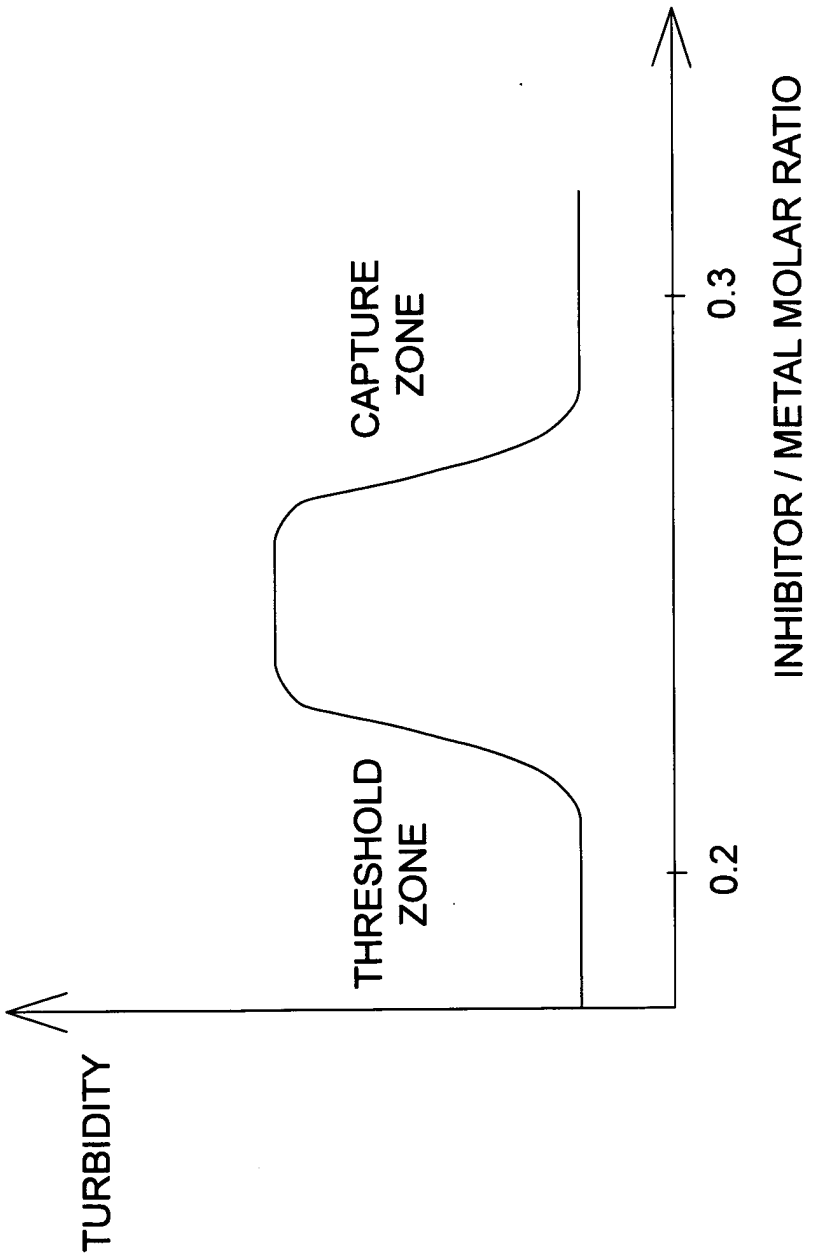


Fig. 2

SPECIFICATION

SHOWING MARKINGS

[[«]]POLYAMINOMETHYLENEPHOSPHONATE DERIVATIVES[[»]]

[[***]]

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to a new class of phosphonates and related salts, the method of preparation of the same and their utilization in the preparation of water additives to be used in different industrial fields. ~~More particularly, the present invention relates to the preparation of products that impart to the water the particular characteristics needed for its utilisation.~~ More specifically, the products and the processes according to the present invention ~~make available~~provide new additives that prevent the segregation of solids from their aqueous solutions or dispersions by acting as precipitation inhibitors and dispersants.

[0003] 2. Description of Related Art

~~The present invention will be here described with particular reference to the preparation and to the use of the products and processes for the preparation and the stabilization of aqueous dispersions, even though its scope should not be limited to those possible applications of the invention described above.~~

[0004] ~~It is known that water found in the~~Water in its natural state, ~~(apart from rainwater) in the form of~~as found in rivers, lakes and seas, and with the exception of rain water, contains a certain quantity of metal ions and anions of different types and in various proportions, ~~depending on~~according to their origins.~~; such~~Such metal ions ~~can lead to~~cause the formation of a precipitate, when water taken from [[a]]its natural environment is used for industrial purposes. ~~In this conditions~~In industrial processes, water which is normally in equilibrium with the external environment is affected by different physical-chemical conditions, and if the concentration of salts ~~in~~under these new conditions exceeds the solubility product ("supersaturation"), ~~their~~salt precipitation is observed ~~during the utilisation~~.

[0005] ~~Salts showing this phenomenon~~Such precipitating salts are generally formed by earth-

alkali metals (Ca; Ba; Mg); among them Calcium -- mostly as carbonate but also as sulfate -- is ~~the main~~mostly responsible for ~~the~~ phenomena of incrustation in several industrial water applications.

[0006] The incrustation (not only limited to poory soluble salts) is generally called "SCALE" by water treatment experts.

[0007] Several factors ~~are responsible for~~cause [["]]supersaturation[["]] and thus ~~for~~ the precipitation of aqueous solutions containing calcium carbonate. The $CaCO_3$ / CO_2 / H_2O system is described schematically here[[:]] in Fig. 1.

[0008] Calcium is present in all surface waters in the form of soluble bicarbonate (HCO_3^-) ~~because of~~due to the absorption of carbon dioxide from the atmosphere. Any modification of such a system leads, in a more or less marked way, to precipitation of ~~the~~ $CaCO_3$.

[0009] The causes for the precipitation of $CaCO_3$ ~~are different and~~ can be classified as follows:

[0010] 1. Concentration of the solution (evaporation of the aqueous phase);

[0011] 2. ~~Variation~~ Variations of ~~the~~ temperature. By heating, the following transformation ~~$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O$~~ takes place[[.]]:

$$Ca(HCO_3) \rightarrow CaCO_3 + CO_2 + H_2O$$

[0012] 3. Variations of the pH. An increase ~~of~~ in the pH of the system results in the following transformation:

$$Ca(HCO_3)_2 + 2\ OH^- \rightarrow CaCO_3 + CO_3^{--} + 2\ H_2O$$

[0013] As far as cooling and/or heat-exchanger circuits [[is]]are concerned, the incrustation (scale) formation mechanism can be attributed to a precipitation of salts from supersaturated solutions in the ~~region~~ regions adjacent to the heat exchange surface of the system.

[0014] The effects of such uncontrolled precipitation are sometimes disastrous. For example, in cooling systems, where large volumes of water are used, the deposits of $CaCO_3$ accumulate in ~~big~~ large quantity in the pipes, causing a reduction of the thermal exchange capacity and leading to a virtual occlusion of the pipes, making it necessary ~~the removal of~~to remove the deposits by acidic treatment with consequent shutdown of the plant.

[0015] Moreover, the formation of a $CaCO_3$ incrustation facilitates the incorporation of solid

particles that cannot be chemically removed (e.g. SiO_2) or the growth of bacteria and algae.

[0016] In order to overcome these disadvantages, pretreatments have been proposed[[:]] in the prior art that ~~they~~ provide for the preventive elimination of low-solubility salts by ionic exchange, precipitation, or by the use of suitable "sequestering agents" and suitable "scale inhibitors".

[0017] Preventive elimination is in most cases not economically acceptable because of the large volumes of water involved.

[0018] The same can be said for the chelating agents; it is well known that these substances ~~forms~~ form water-soluble complexes with the metal ions~~, in~~ within a well defined stoichiometric molar ratio.

[0019] The preferred treatment ~~today~~in the prior art involves ~~for~~ the use of suitable "scale inhibitors" ~~using~~ that take advantage of the so called "Threshold Effect." The Threshold Effect was discovered by observing the ~~behaviour~~ behavior of inorganic polyphosphates that prevent the precipitation of the $CaCO_3$ from supersaturated solutions by means of sub-stoichiometric concentrations (Hatch and Rice, *Indust. Eng. Chem.*, 31, 51-53 (1939); Reitemeier and Buehrer, *J. Phys. Chem.*, 44 (5), 535-536 (1940); Fink and Richardson U.S. Pat. No. 2,358,222; and Hatch, U.S. Pat. No. 2,539,305).

[0020] The mechanism by which [[the]] precipitation is inhibited is not completely understood today, although the ~~adsorption~~ absorption of an inhibitor onto the crystalline surface seems necessarily to be the first step in the inhibition process. The molecules of the inhibitor are attracted on the growing crystalline surface by the presence of metal cations such as Ca, Mg, Ba, for which they have a great affinity.

[0021] Once the molecules of the inhibitor are adsorbed, ~~they locate~~such molecules reside on the surface of the crystal, thus disturbing the regularity of its growth.

[0022] If all of this happens ~~in~~during the "nucleation" phase, i.e. ~~in~~during the stage in which a certain number of molecules in solution ~~begin~~ begins to aggregate in order to give rise to a crystal nucleus, the inhibitor can disturb nuclear growth to such an extent as to make the nucleus redissolve.

[0023] Such ability, exercised by various polyelectrolytes, is particularly marked in the case of phosphonates, which moreover combine corrosion inhibition functions with great resistance to

hydrolysis.

[0024] However, for every operating condition, there is a limit to the molar ratio between inhibitor and metal. In fact, by increasing the phosphonate quantity beyond a certain limit, precipitation of insoluble calcium salts of phosphonates is observed; in such "turbidity" zone, the phosphonate is no longer active. The effectiveness of the phosphonates at various inhibitor/metal ratios is shown schematically in ~~figure 1, where~~Fig. 2, wherein the x-axis ~~reports~~relates to the molar ratio between metal and inhibitor, while the y-axis ~~reports~~relates to the turbidity measured nephelometrically.

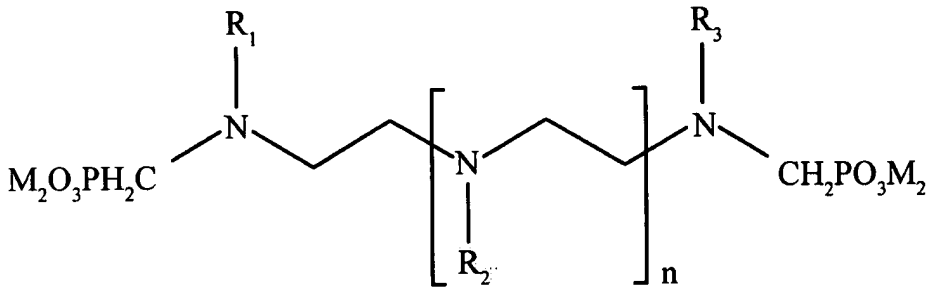
[0025] Furthermore, it is well known that it is necessary to provide for more ~~critical~~ effective recovery cycles of industrial water -- above all because of an increasing use of water resources -- in order to reduce both the quantity of water used and the environmental impact of the treatment agents.

~~**Summary of the invention**~~

BRIEF SUMMARY OF THE INVENTION

[0026] The present invention relates to a new class of phosphonates, to a simple and economic process for the production of said new class of phosphonates, and to the use of said phosphonates in water treatment applications. Therefore, the main object of the present invention is a new class of phosphonates that can be used for water treatment.

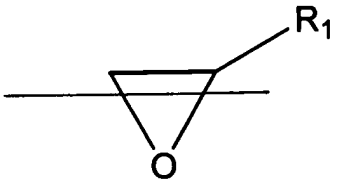
[0027] The compounds that form the object of the present invention are the derivatives of polyaminomethylenephosphonates having the following general formula:



where *n* is preferably a number ~~an integer~~ between 2 and 15000, most preferably between 2 and 50; wherein M is hydrogen or a cation, wherein R_1, R_2, and R_3 are each independently

selected from the group consisting of $CH_2PO_3M_2$, CH_2R_4, wherein R_4 is $CHOHCH_3$, $CHOHCH_2Cl$, or $CHOHCH_2OH$, $(CH_2)_mSO_3M$, wherein m is 3 or 4, and $CH_2CH_2R_5$, wherein R_5 is $CONH_2$, CHO, $COOR_6$, COOX, or CN, wherein R_6 is CH_3 or C_2H_5, and wherein X is analkali metal or ammonium, and wherein at least one of R_1, R_2, and R_3 is not $CH_2PO_3M_2$.

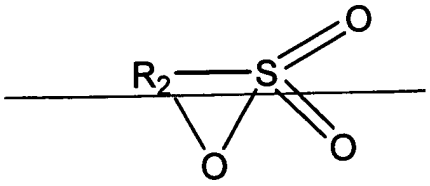
~~M_2 may be hydrogen or a suitable cation and each R group may be a CH_2-PO_3M_2[[,]] group, or a linear or branched alkyl residue resulting from the reaction of the groups with the following reagent classes:~~



~~1)~~

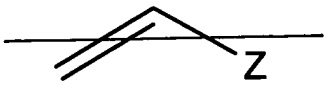
~~where R^1 may be H, CH_3, CH_2Cl, CH_2OH~~

~~2)~~



~~where R_2 is an alkyl with the number of carbon atoms between 3 and 5[[.]]~~

~~3)~~



~~where Z is a group from among: $CONH_2$, CHO, $COOR_3$ COOX, CN, where R_3 = CH_3, C_2H_5, and where X = H, Na, K, NH_4.~~

[0028] ~~In Particular~~More particularly, the compounds that form the object of the present invention are ~~the~~ derivatives of polyaminomethylenephosphonates according to the above mentioned formula, ~~where~~ wherein the polyamine chain may be linear or branched, ~~and where~~

wherein n is an integer or fractional integer which is, or on average is, from about 2 to about 15000[[:]], wherein M_2 may be hydrogen or a suitable cation such as alkali metal or ammonium, and ~~where~~ wherein each R group my be the same or different and is independently selected from the following classes:

[0029] 1. $CH_2PO_3M_2$, ~~where~~ wherein M may be hydrogen or a suitable cation such as alkali metal or ammonium;

[0030] 2. CH_2R, ~~where~~ wherein R = CH_2OH; $CHOHCH_3$; $CHOHCH_2Cl$; $CHOHCH_2OH$;

[0031] 3. $(CH_2)_nSO_3M$, ~~where~~ wherein n = ~~3÷4~~ 3-4, and where M may be hydrogen or a suitable cation such as alkali metal or ammonium;

[0032] 4. CH_2CH_2R, ~~where~~ wherein R = $CONH_2$, CHO, $COOR_1$, COOX, CN ,where R_1 = CH_3÷C_2H_5, and ~~where~~ wherein X may be hydrogen or a suitable cation such as alkali metal or ammonium,

[0033] with the condition that at least one of substituent R should be different from the methylenephosphonated group (i.e.: other than $-CH_2PO_3M_2$).

[0034] A particular advantage of ~~this new~~ the class of phosphonates[[,]] that are the object of this invention[[,]] is that such compounds do not show "Turbidity Zone" and are, therefore, to be considered non ~~Calcium-sensitive~~calcium-sensitive at any concentration and temperature tested.

[0035] ~~; they~~ These compounds are also effectives at high pH values (>10).

[0036] This is a very important aspect of the invention, since calcium tolerance of the traditional scale inhibitors like HEDP or ATMP quickly reduces with an increasing of the pH; in particular, this is important today because water treatment processes are carried out at higher pH values than in the past. In fact, a higher pH reduces the effects of corrosion, which is more marked at lower pH values.

[0037] The advantages of the~~this~~ new class of phosphonates[[,]] that are the object of ~~this invention, that~~ the present invention can be summarised as follows:

[0038] 1. ~~Threshold Effect,~~A threshold effect that is typical of the phosphonates, i.e. inhibition of precipitation from solutions supersaturated with $CaCO_3$ and/or $CaSO_4$ at sub-stoichiometric concentrations of the inhibitor[[.]];

[0039] 2. Non calcium-sensitivity,[[:]] because increases in pH and concentration of calcium strongly affect the tolerance of the standard phosphonates (HEDP, ATMP, etc.) to

calcium, increasing the possibility of precipitation of poorly soluble calcium-phosphonate salts.

[0040] 3. ~~Dispersing Effect:~~ A dispersing effect better than ~~the~~ traditional phosphonates. This new class of phosphonates behaves like ~~the~~ acrylic polymers~~. They act~~, accting as dispersants and deflocculants, and stabilizing colloidal systems which remain steadily dispersed for long periods.

[0041] 4. ~~Corrosion Inhibition:~~ A corrosion inhibition that is comparable to that of the standard phosphonates.

[0042] 5. ~~Chelating Effect:~~ A chelating effect that is comparable to that of the standard phosphonates.

[0043] 6. ~~Hydrolitic Stability:~~ A hydrolytic stability that is similar to conventional phosphonates.

[0044] As shown in point 3) above, in addition to the threshold effect, the products object of the present invention shows a high "dispersing ability". This property ~~became~~ becomes evident when the sequestering power is determined by the traditional "HAMPSHIRE" method, and by using ~~: with~~ this method it is not possible to identify an end-point during the titration with calcium acetate.

[0045] This property also suggests a potential application ~~of~~ for this new class of phosphonates as deflocculants, to be used in a certain number of processes and applications where ~~they are involved as stabilizers~~this new class of phosphonates can act as a stabilizer for different ~~kind~~ knds of dispersions like pigments (TiO_2), kaolin and drilling mud, and in the industrial and domestic detergent field for their ability to disperse dirt particles. From a general point of view, ~~thanks to~~because of their particular properties, the products according to the present invention can be used for:

[0046] a reverse osmosis system;

[0047] scale removal;

[0048] scale prevention and corrosion control;

[0049] boiler cleaning;

[0050] bottle washing;

[0051] hard surface cleaners;

[0052] cooling system;

[0053] slurry dispersion;

[0054] textile processing;

[0055] sanitary cleaners;

[0056] paints;

[0057] secodnary oil recovery;

[0058] oil drilling muds;

[0059] laundry detergents;

[0060] industrial cleaners;

[0061] peroxide stabilisation;

[0062] metal finishing;

[0063] metal cleaners;

[0064] geothermal water;

[0065] ~~set retardens~~ setting retardants for concrete;

[0066] pulp & paper bleaching;

[0067] car ~~wash~~washing;

[0068] flash desalination.

[0069] ~~Obyect~~ An object of the present invention is also a simple and economic process for the preparation of the phosphonates and their ~~utilisation~~ utilization in the ~~abovesaid~~ above mentioned fields, particularly as inhibitors of the formation, deposition, and adhesion of incrustations caused by insoluble salts of alkali-earth metals, in particular Ca^{++}[[,]] and Mg^{++}, on metal surfaces of aqueous equipment systems (cooling towers, boilers, gas scrubbers, etc.)

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0070] Fig. 1 is a schematic illustration of a supersaturation cycle.

[0071] Fig. 2 is a chart illustration of the effectiveness of phosphonates as nuclear growth inhibitors at various inhibitor/metal ratios.

DETAILED DESCRIPTION OF THE INVENTION

[0072] Detailed descriptions of embodiments of the invention are provided herein. It is to be understood, however, that the present invention may be embodied in various forms. Therefore, the specific details disclosed herein are not to be interpreted as limiting, but rather as a representative basis for teaching one skilled in the art how to employ the present invention jn virtually any detail system, structure, or manner.

[0073] More specifically, embodiments of the present invention will now be described with particular reference to the preparation and to the use of products and processes for the preparation and the stabilization of aqueous dispersions, even though the scope of the invention should not be limited to such possible applications.

[0074] ~~The compounds object of this invention is~~In one embodiment of the invention, polyaminomethylenephosphonate derivatives are prepared by a phosphonomethylation reaction of polyamine or mixtures of polyamines[[,]] by means of the Mannich reaction illustrated hereunder[[.]]:

$$-NH + HCHO + H_3PO_3 \xrightarrow[\Delta]{HCl} -NH_2P(=O)(OH)_2$$

[0075] The phosphonomethylation reaction of amines according to Mannich is described in the literature, eg: K. Moedritzer and R. Irani, *J. Organic. Chem.* 31 (5) 1603-7.~~: any relevant reference is to be considered mentioned herein to fully complete the invention specifications.~~

[0076] A typical procedure provides for the amine to be slowly added to a mixture of a phosphorus-based acid and hydrochloric acid. The reaction mixture thus obtained is heated to reflux with the addition of formaldehyde. The reaction time can vary from 1 to 5 h.

[0077] The derivatives of the polyaminomethylenephosphonate ~~object of this invention~~in this embodiment are added to the aqueous systems in quantities between 2 and 50 mg/l, in order to inhibit precipitation, deposition and adhesion of scale, especially of $CaCO_3$.

[0078] ~~The expression "inhibits precipitation and formation of deposits"~~Inhibiting the precipitation and formation of deposits includes the threshold effect, dispersion, solubilization or modification of the precipitate's morphology. ~~The expression "inhibits the adhesion"~~Inhibiting

adhesion defines just that scale is easily removed, e.g. by simple washing/rinsing and not by mechanical or chemical treatment, ~~not being~~because the incrustation is not strongly bonded to the underlying surface ~~to which it adheres~~.

[0079] The term "scale" includes incrustation formed by $CaCO_3$, $CaSO_4$, $BaSO_4$ ~~deposit~~ deposits and can be extended in a generalized manner to include all low-solubility salts of several cations (Mg, Fe, ~~ecte~~etc.).

[0080] The term "aqueous systems" refers to industrial and/or commercial systems that use water in heat-exchange processes and includes cooling towers, boilers, desalination systems, gas scrubbers; furthermore, processes of desalination by ~~Reverse Osmosis~~reverse osmosis (RO) are included.

[0081] Of particular importance are systems operating in severe conditions, such as high pH and high concentrations of calcite ($CaCO_3$). The preparation and the application of the polyaminomethylenephosphonate derivatives ~~object of the present invention~~according to the present embodiment are illustrated in the following examples, which will clarify their applications, but without ~~however~~ limiting the scope of the invention.

[0082] EXAMPLE 1

[0083] Into a suitable reaction vessel 350-g of triethylenetetramine were charged; thereafter the reaction mixutre was heated at ~~90°÷95°C.~~90-95°C.

[0084] Ethylene oxide was than added stepwise at such a rate that, with external cooling applied, the temperature did not exceed 100°C.

[0085] 211 g of ethylene oxide ~~had been~~were added over a period 1½ hours. The resultant product was then converted in the phosphonomethylated derivates according to Mannich's reaction.

[0086] With the same synthetic path is possible to obtain β hydroxyethyl derivates of linear or branched polyamines or a mixture ~~of them in a right~~ thereof with an appropriate ratio. Other compounds ~~of these invention~~according to the present embodiment can be prepared according to the above described procedure ~~above describe~~ by using propylene oxide instead of ethylene oxide (β hydroxy propyl derivates).

[0087] EXAMPLE 2

[0088] Into a suitable reaction vessel 292 g of triethylenetetramine were charged.

[0089] Under stirring conditions, acrylonitrile was than added stepwise at such a rate that, with external cooling applied, the temperature did not exceed 50°C.

[0090] 212 g of acrylonitrile ~~had been~~were added over a period 2 hours. The resultant product was than converted ~~in the~~into phosphonomethylated derivates according to Mannich's reaction.

[0091] With the same synthetic path is possible to obtain β cyanoethyl derivates of linear or branched polyamines or mixture ~~of them in a right~~thereof with an appropriate ratio.

[0092] EXAMPLE 3

[0093] Into a suitable reaction vessel 292 g of triethylenetetramine were charged.

[0094] Under stirring, 488 g of 1,3-propane sultone, dissolved in 1140 g of methanol, was added dropwise at a tempearture between ~~40°÷50°C~~40-50°C. After 2 hours, the methanol was removed by evaporation to dryness and the residue dissolved in water. The resultant product was than converted ~~in the~~into phosphonomethylated derivates according to Mannich's reaction.

[0095] With the same synthetic path is possible to obtain N-(sulfo propane)amino ~~derivates~~ derivatives of linear or branched polyamines or ~~mixutre of them in a right~~a mixture thereof with an appropriate ratio.

[0096] Other compounds ~~of these invention~~according to the present embodiment can be prepared according to the above described procedure ~~above describe~~ by using epichlorohydrin or other different oxiranes ~~derivates~~ derivatives instead of 1,3 propane sultone.

[0097] EXAMPLE 4

[0098] Into a suitable reaction vessel 234 g of compound of example 1 were added to a 70% a phosphorus-based acid solution (478 g) ~~and~~ as well as 32% of hydrochloric acid (342 g). The mixture thus obtained was heated to reflux, 340 g of 37% aqueous formaldehyde solution ~~was~~ were added dropwise in the course of ~~ea~~ about 1 hr, and the reaction mixture was kept at the reflux temperature for 1 additional hr. 300 g ~~volatiles~~of volatile substances ~~was~~were then removed from the reaction mixture by distillation. The final product obtained was a viscous fluid

having an active substance of 50%. Infrated analysis of the product showed the presence of methylenephosphonic amine groups, while P^{31} NMR analysis ~~indicate~~ indicated that at least 90% of the amine groups had been phosphonomethylated. The impurities ~~include~~ included unreacted phosphorus-based acid, phosphoric acid and other unidentified compounds.

[0099] By following the same synthetic method, ~~it is possible to obtain~~ phosphonometilated ~~derivates~~ derivatives of polyamine may be obtained or a mix of polyamine having an R group selected from the following class:

[0100] 1. $CH_2PO_3M_2$, ~~where~~wherein M may be hydrogen or an suitable cation such as alkali metal or ammonium;

[0101] 2. CH_2R, ~~where~~ wherein R = CH_2OH; $CHOHCH_3$; $CHOHCH_2Cl$; $CHOHCH_2OH$

[0102] 3. $(CH_2)_nSO_3M$, ~~where~~ wherein n = 3÷4 where M may be hydrogen or a suitable cation such as alkali metal or ammonium;

[0103] 4. CH_2CH_2R, ~~where~~ wherein ~~WR~~ R = $CONH_2$, CHO, $COOR_1$, COOX, CN, ~~where~~wherein R_1 = CH_3÷C_2H_5, and wherein ~~where~~ X may be hydrogen or a suitable cation such as alkali metal or ammonium[[.]],

~~where~~ wherein preferably at least one or more than one substituent R is different from the methylenephosphonated group.

[0104] EXAMPLE 5

[0105] This example is related to the threshold effect ~~Threshold Effect~~ on $CaCO_3$ at pH = 10, T = 70°C, 100 ppm of $CaCO_3$

[0106] ~~The~~ This method describes the procedure for the determination of the~~Threshold Effect~~threshold effect, that is, the ability of a dispersing agent, present in substoichiometric amounts, to inhibit the precipitation of solutions supersaturated with calcium carbonate in deionized water.

[0107] This method measures the efficiency of a dispersant by titration of the ~~Calcium~~ calcium ion remaining in a solution supersaturated with $CaCO_3$ respectively before and after treatment in an oven at 70°C. The greater the calcium concentration after the period in the oven, the greater the efficiency of the dispersant in preventing precipitation of the $CaCO_3$.

[0108] Increasing substoichiometric amounts of phosphonate are dissolved in solutions contaning [Ca^{++}] and [CO_3^{--}] obtained by mixing ~~proper~~ suitable $CaCl_2$ and Na_2CO_3 solutions.

[0109] The precipitation of calcium carbonate is measured by titration of the filtered solution. The results obtained are summarised in ~~table~~ Table 1.

[0110] Table 1

[0111] Operating Conditions: 100 ppm $CaCO_3$; pH = 10; T = 70°C; 24 h

[0112] Inhibition %

Inhibitor	**~~0,25~~0.25 ppm**	**~~0,5~~0.5 ppm**	**1 ppm**
Example 4	72	97	99
HEDP	74	99	100
ATMP	75	99	100
DTPMP	65	85	100
PBTC	90	100	100

[0113] wherein:

[0114] HEDP = Hydroxy-ethylydene-1,1-diphosphonic Acid;

[0115] ATMP = Amino-tris Methylenephosphonic Acid ;

[0116] DTPMP = Diethylenetriamine penta (methylenephosphonic acid);

[0117] PBTC = Phosphono Butane tris Carboxylic Acid.

[0118] EXAMPLE 6

[0119] This example relates to the $CaCO_3$ ~~Threshold Effect~~threshold effect at pH = 11.5, T = 40°C, 400 ppm of $CaCO_3$

[0120] Following the method described in example 5, the following results were obtained:

[0121] Table 2

[0122] Operating Conditions: 400 ppm $CaCO_3$; pH = 11,5; T = 40°C; 24 h

[0123] Inhibition %

Inhibitor	40 ppm	80 ppm	200 ppm	400 ppm	450 ppm
Example 4	0	35	90	92	95
ATMP	0	35	40	60	65
DTPMP	0	35	83	80	80
PBTC	0	30	42	92	95

[0124] EXAMPLE 7

[0125] This example relates to $CaSO_4$ ~~Threshold Effect~~ threshold effect at pH = 7; T= 70°C; 6800 ppm of $CaSO_4$.

[0126] Following the method described in example 5[[.]], ~~In the specific case~~ the solution of $CaSO_4$ was prepared starting from $CaCl_2$ and Na_2SO_4. The results obtained are summarized hereunder ~~summarised~~:

[0127] Table 3

[0128] Operating Conditions: 6800 ppm $CaSO_4$; pH = 7; T = 70°C; 24 h

[0129] Inhibition %

Inhibitor	~~0,5~~0.5 ppm	1 ppm	2 ppm	5 ppm	10 ppm
Example 4	10	10	90	100	100
DTPMP	10	22	75	95	100

[0130] EXAMPLE 8

[0131] This example relates to $CaSO_4$ ~~Threshold Effect~~threshold effect at pH = 7; T = 70°C; 6800 ppm of $CaSO_4$ + 6000 ppm of Ca^{++}.

[0132] Following the method described in example ~~4. In the specific case the,~~ a solution of $CaSO_4$ was prepared starting from $CaCl_2$ and Na_2SO_4. The results obtained are ~~summarised~~

summarized in ~~table~~Table 4.

[0133] Table 4

[0134] Operating Conditions: 6800 ppm $CaSO_4$ + 6000 ppm di Ca^{++}; pH = 7; T = 70°C; 24 h

[0135] Inhibition %

Inhibitor	**2 ppm**	**5 ppm**	**10 ppm**
Example 4	15	91	99
DTPMP	22	45	96

[0136] EXAMPLE 9

[0137] This example relates to $CaSO_4$ ~~Threshold Effect~~threshold effect at pH = 7; T = 90°C; 6800 ppm of $CaSO_4$.

[0138] Following the method described in example 5~~. In the specific case, the,~~ a solution of $CaSO_4$ was prepared starting from $CaCl_2$ and Na_2SO_4.The results obtained are ~~summarised~~ summarized in ~~table~~Table 5.

[0139] Table 5

[0140] Operating Conditions: 6800 ppm $CaSO_4$; pH = 7; T = 90°C; 24 h

[0141] Inhibition %

Inhibitor	**~~0,5~~0.5 ppm**	**1 ppm**	**2 ppm**	**5 ppm**	**10 ppm**
Example 4	0	5	18	85	99
DTPMP	0	0	5	73	90

[0142] EXAMPLE 10

[0143] This example relates to $CaSO_4$ ~~Threshold Effect~~threshold effect at pH = 7; T= 90°C; 6800 ppm of $CaSO_4$ + 6000 ppm of Ca^{++}.

[0144] Following the method described in example 5~~. In the specific case, the,~~ a solution of $CaSO_4$ was prepared starting from $CaCl_2$ and Na_2SO_4. The results obtained are ~~summarised~~ summarized in ~~table~~Table 6.

[0145] Table 6

[0146] Operating Conditions: 6800 ppm $CaSO_4$ + 6000 ppm di Ca^{++}; pH = 7; T = 90°C; 24 h

[0147] Inhibition %

Inhibitor	**~~0,~~50.5 ppm**	**1 ppm**	**2 ppm**	**5 ppm**	**10 ppm**
Example 4	10	15	18	91	99
DTPMP	0	0	8	38	45

~~**Calcium-Sensitivity**~~

[0148] EXAMPLE 11

[0149] This example relates to calcium-sensitivity. The Grace "CLOUD POINT TEST" was used for testing the calcium-sensitivity. This simple method allows calcium-sensitivity to be verified visually by estimating the turbidity point of an inhibitor solution in a concentrated calcium solution. The inhibitor is added at increasing amounts to hard water having the following characteristics: 500 ppm of Ca^{++} (as $CaCl_2$), pH = 8.3 (0.05 M of ~~Boric~~ boric buffer), at a temperature of 60°C and 100°C for 24 h.

[0150] The turbidity of solutions after 24 hours was observed. The observation ~~confirmis~~ confirmed that the turbidity is greater at increasing amounts of inhibitor. The results obtained are ~~summarised in table~~ summarized in Tables 7 and 8.

[0151] Table 7

[0152] 500 ppm $CaCO_3$; pH = ~~8,3~~8.3; T = 60°C

[0153] Inhibitor Dose

Inhibitor	**10 ppm**	**30 ppm**	**50 ppm**	**100 ppm**
Example 4	clear	clear	clear	clear
ATMP	clear	turbid	precipitate	precipitate

[0154] Table 8

[0155] 500ppm $CaCO_3$; pH = ~~8,3~~8.3; T = 100°C

[0156] Inhibitor Dose

Inhibitor	**10 ppm**	**30 ppm**	**50 ppm**	**100 ppm**
Example 4	clear	clear	clear	clear
AMTP	precipitate	precipitate	precipitate	precipitate

~~**Fe^{3+} Sequestering**~~

[0157] EXAMPLE 12

[0158] This example relates to Fe^{3+} sequestering. The measurement of the sequestering power of iron is difficult both for traditional phosphonates and for the polyaminomethylenephosphonate derivatives~~, object of this invention:~~ according to the present embodiment, because both products have considerable dispersing ability, and if we considerer the colloidal aspect of the ferric hydrate, it is clear how difficult it could be to distinguish between the dispersed iron and the iron effectively sequestered~~; it.~~ It is well known that a very fine dispersion is very similar to a solution. It must be said that often, in practical applications, an effective dispersion is as useful as a true sequestration.

[0159] The method ~~consists in~~ involves the addition of a known quantity of solution of ferric ions to an aqueous solution of inhibitor at constant pH. After 24 hours under agitation, the aspect of the sample is evaluated. The samples where a precipitate is present after 24 hours of agitation ~~are~~ were considered "precipitated," and so the first clear sample ~~has been~~was considered in order to attribute a sequestring value. The results obtained are summarised in ~~table~~ Table 9.

[0160] Table 9

[0161] Fe^{3+} ~~Sequestering Power~~ sequestering power expressed as mg Fe^{3+} /g of product

Inhibitor	pH = 5	pH = 6	pH = 7	pH = 8	pH = 9	pH = 10	pH = 11	pH = 12
Example 4	0	60	180	200	260	360	200	20
HEDP	240	280	320	360	800	800	1200	1200
ATMP	40	60	100	120	140	180	120	0
DTPMP	40	60	80	140	220	130	60	20

[0162] ~~These~~ The above data should be carefully evaluated, because the method ~~utilised~~utilized does not allow a dispersion to be distinguished from a true chelation~~; however,~~. However, an internal comparison ~~indicate~~ indicated that traditional phosphonates and the derivatives object of the present invention ~~are~~ were equally effective in the control of ferric ion.

~~**Corrosion Inhibition**~~

[0163] The present invention further addresses the problem of corrosion inhibition.

[0164] The corrosion of metal equipment is an almost universal problem for aqueous systems~~: on a metal surface two~~. Two distinct areas coexist on a metal surface, an anode and a cathode, which ~~in practice~~ may be situated very close to each other and set up an electrical circuit with consequent Redox reactions leading to the solubilization of the metals. ~~In particular~~MOre particularly, iron surfaces are transformed into water-soluble $Fe^{2+/3+}$ ions. The corrosion, and therefore the loss of metal from part of the structure, takes place only in the anodic zone.

[0165] Without entering into the detail of the corrosion phenomenon, it is clear, however, that the damage caused by corrosive phenomena can be considerable in extent. Various methodologies and various products have been developed ~~in the time to solve~~over time to address the problems related to the entity and various origins of ~~the~~ corrosive phenomena. One of the more widespread methodologies involves the use, in aqueous phase, of suitable "corrosion inhibitors". These compounds ~~which can~~may be organic or inorganic films or protective barriers between the metal surface and the of corrosion medium. ~~This~~ Such a protective film ~~formed~~ can be developed by the following means:

[0166] a. *Precipitation* of an inhibitor onto the metal surface;

[0167] b. *Passivation* of the metal surface;

[0168] c. *Adsorption* of an inhibitor onto the metal surface through the electronic lone pair ~~of some~~ a donor ~~elements~~ element (N, S, O, P).

[0169] EXAMPLE 13

[0170] In the following example, a simple test is described for ~~the evaluation of~~evaluating the efficiency of the compounds ~~object of this invention~~according to the present embodiment as corrosion inhibitors. The operating conditions and the procedure used in the test are indicated below:

[0171] ~~Take a~~Taking water with 30 French degrees of hardness, ~~brought~~ bringing it at pH = 8.5 with diluted NaOH and than ~~add~~adding the desired quantity of inhibitor.[[]];

[0172] ~~Add~~ Adding carefully cleaned and weighed steel coupons to the solution.

[0173] The test lasts 5 days with a constant airflow bubbled through the solution.

[0174] After 5 days, ~~weigh~~ weighing the test pieces and estimating the loss in weight ~~is estimate~~.

[0175] The results obtained are summarised in the following table:

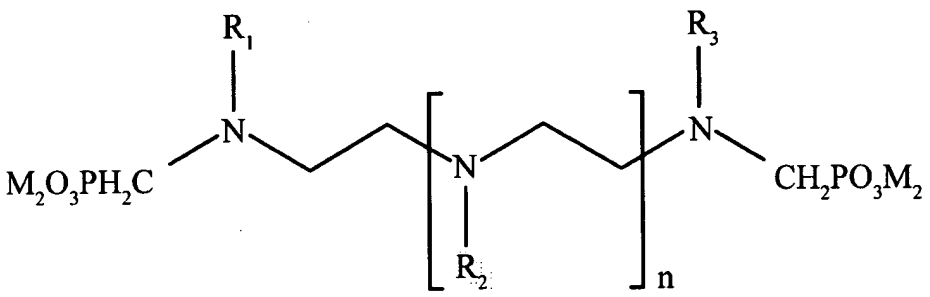
[0176] Table 10

Inhibitor	% weight loss after 5 days
Example 4	0,25 0.25
ATMP	~~0,45~~ 0.45
HEDP	~~0,3~~ 0.3
Blank	~~0,7~~ 0.7

~~SUMMARY~~ABSTRACT

[0177] ~~A new class of polyaminopghosphonate derivatives usable as inhibitors of precipitation and dispersants in aqueous systems. The products in object have complete tolerance of calcium and can be employed in severe conditions of use in the water treatment and detergent fields.~~

In one embodiment, a scale inhibitor comprising at least one polymethylenephosphonate derivative having the following formula:



wherein n is a number, wherein M is hydrogen or a cation, wherein R_1, R_2, and R_3 are each independently selected from the group consisting of $CH_2PO_3M_2$, CH_2R_4, wherein R_4 is $CHOHCH_3$, $CHOHCH_2Cl$, or $CHOHCH_2OH$, $(CH_2)_mSO_3M$, wherein m is 3 or 4, and $CH_2CH_2R_5$, wherein R_5 is $CONH_2$, CHO, $COOR_6$, COOX, or CN, wherein R_6 is CH_3 or C_2H_5, and wherein X is an alkali metal or ammonium, and wherein at least one of R_1, R_2, and R_3 is not $CH_2PO_3M_2$. In another embodiment, a method for inhibiting scale formation in water, and in still another embodiment, a method for sequestering iron ions in a water systems, each of the methods comprising the step of providing the water with the above described polymethylenephosphonate derivative.